The present disclosure describes piperazine amphotheric surfactants made by combining N-propyl-N-piperazine, N-hydroxypropyl piperazine, N-aminopropyl piperazine, and N,N'-aminopropyl piperazine with a high molecular weight fatty acid, such as oleic acid, tall oil fatty acid, coconut fatty acid, or sebacic acid, followed by reaction with acrylonitrile or methacrylate. Then the resultant compound is saponified.

The final product may be used in shampoos, in soaps, for textile scouring, and for other uses.

The present application relates to novel surfactants, and it particularly relates to a high molecular weight fatty heterocyclic surfactant having high effectiveness in a wide variety of acidities and alkalitivities.

It is among the objects of the present invention to provide a highly effective detergent which will maintain a high fine bubble foam over long periods of time in textile processing, without deterioration or loss of effective foam properties and without decreasing the volume of the foam regardless of the change in pH, whether it become strongly acid or become strongly alkaline, regardless of the salts that may be present or the pH of the bath in which the foam is being produced, and which will have unusually high corrosive inhibiting properties and which may be widely utilized in metal processing such as electroplating, radiator liquids, and coolants for metal working processes.

The preferred oil and water soluble surface active compounds have the following general formula:

\[
\text{CH}_2\text{CH}_2\text{CON} R_1 \text{N-R_2-X-} R_3 \text{COOH}
\]

where \(R_1\) represents a hydrocarbon or alkyl group containing from 7 to 21 carbon atoms, and where \(R_2\) may be replaced by \(R_3\) and where \(R_3\) represents a short chain hydrocarbon or alkyl groups containing 1 to 6 carbon atoms, and \(X\) represents either oxygen or nitrogen taking the form of an ether or secondary or tertiary amine linkages.

The alkali metal salts of these fatty complexes are water soluble and are versatile adjuncts in such diverse fields as cosmetic and shampoo preparations, industrial and household cleaners, detergent and scouring agents for processing textiles, emulsifiers and corrosion inhibitors.

These compounds are anionic in basic solution and cationic in acid solution; and in the range of pH 5.0 to 9.0, they exhibit both cationic and anionic properties, being truly amphoteric.

As fatty heterocyclic nitrogen carboxylic acids, they are soluble in polar and non-polar solvents, and may be neutralized with amines to form oil soluble salts. Both the carboxylic acids and their amine salts are excellent film forming compounds, exhibiting outstanding corrosion inhibiting properties.

They are effective as petroleum additives, detergents, asphalt wetting and anti-stripping agents and biocidal agents.

To give the chemical equations which are involved in making the above compounds, coconut fatty acid, oleic fatty acid, tall oil fatty acid, stearic acid or sebacic acid are combined starting at 300° F. and increasing up to 450° F. with an aliphatic long chain piperazine desirably having at least one terminal primary amino group or a short chain hydroxalkyl group.

The polyamine is desirably aminoethyl piperazine or hydroxyethyl piperazine which reacts as set forth in the following equations:

\[
\text{RCOOH} + 2\text{HNCH}_2\text{CH}_2\text{NH} \rightarrow \text{RCO(NH}_2\text{CH}_2\text{CH}_2\text{NH}
\]

\[
\text{RCOOH} + \text{HOCH}_2\text{CH}_2\text{NH} \rightarrow \text{RCO(NCH}_2\text{CH}_2\text{OH}
\]

In the Equations I and II, \(R\) is a fatty group having 8 to 22 carbon atoms and the reaction is desirably carried out starting at about 250° to 350° F. under a low vacuum for one to three hours followed by continuing a reaction at about 300° to 450° F. for four to eight hours at a higher vacuum.

Then to one mol of these heterocyclic compounds is added in dropwise fashion one mol of an acrylic compound, such as acrylonitrile or methyl acrylate at a temperature of 100° to 150° F.

The acrylic compounds should desirably have one unsaturated double bond in the aliphatic chain and contain from one to four carbon atoms, and they have terminal —CN or —COOH groups.

They also may have methylyl, ethyl or propyl groups either as terminal groups or as side chains.

Desirably, a three-neck flask is utilized with a condenser connected to one neck, an agitator connected through the other neck and a funnel and thermometer is connected in the third neck.

The acrylic compound is dropped for about one hour, followed by heating for about one and one-half to three hours at 180° to 230° F. with the final processing and elevated temperature treatment taking place at 15 to 18 inches vacuum.

After this combination, with the acrylic compounds, has been completed, the reaction product is treated with equimolar proportions of caustic soda in 25% concentration and at a temperature of about 200° F. for about one and one-half to three hours.

In these compounds, the R group is desirably derived from oleic acid, tall oil fatty acid or coconut fatty acid and lean desirably from sebacic acid.

They are surprisingly effective as detergents, emulsifiers and corrosion inhibitors in very small concentrations. They may be used in shampoos, in soaps, emulsion polymerization, as oven cleaners, as industrial cleaners, in electroplating, in cosmetics, for textile scouring, dyeing and lubrication, in sanitizers, in paints, and in leather treating.

The piperazine derivatives are synthesized by the reaction of fatty esters, acids or acid chlorides with substituted piperazine compounds as N-aminoethyl piperazine, N-...
3,385,858

hydroxyethyl piperazine, N-aminopropyl piperazine, Nhydroxypropyl piperazine and N,N'-aminomethyl pipera

EXAMPLE I

Into a three-neck two liter flask was charged one mol
of lauric acid and one mol of aminoethoxy piperazine.

The contents was heated to 150°-170° C, until 1 mol
(18 milliliters) of water was recovered in the moisture
trap. The dodecyl amidothyl piperazine was cooled to
60° C. and one mol of methyl acrylate or acrylonitrile
was slowly added through a dropping funnel over a
period of one hour.

The temperature was gradually raised to 100° C., and
held for two hours at which time the addition reaction
was completed. The one mol of sodium hydroxide dis-
solved in 200 milliliters of water was added to the flask
and the mixture heated with stirring at 90°-100° C. until
the nitrile group was completely saponified at which time
the flask was purged with nitrogen to remove all traces
of ammonia and the product was then diluted to 50% active
matter with hot water.

The aqueous solution of the dodecyl amidothyl piper-
azine sodium propionate was a yellow-brown viscous solu-
tion. Dilute solutions showed good stability to acids and
alkalies, high foaming characteristics, excellent detergency
and surfactant properties.

EXAMPLE II

One mol of methyl stearate and one mol of hydroxy-
ethyl piperazine was charged into a three-neck two-liter
flask equipped with a thermometer, agitator and receiving
trap.

The mixture was heated to 175° C. and held at this
temperature until one mol of methyl alcohol was
recovered in the receiver.

The flask was then cooled to 60° C. and five grams of
a 25% solution of sodium methyleate in methyl alcohol
was added as catalyst followed by one mol of methyl-
acrylate over a period of one hour.

The temperature was then raised to 75° C. and held
at this temperature until test samples showed complete
reaction between the hydroxy group and the methyl
acrylate to form the ethoxy methyl propionate.

The sodium salt was formed by the saponification of
the methyl ester with 20% caustic soda (200 grams) at
100° C. The resulting compound is a white paste, soluble
in water and stable to acids and alkalies.

It showed good scouring and foaming properties on
all types of fabrics and left the fabrics with a nice soft
hand (finish). It showed good emulsifying properties and
made stable mineral oil emulsions of the O/W type.

The methyl acrylate adducts of these long chain hetero-
cyclic nitrogen compounds are oil soluble surfactants.
They are dispersible in water, lowering the surface tension
of water to 30 dynes/centimeter at 0.1 concentration.

The compounds are completely soluble in alcohols,
ketones, ethers, and aromatic and aliphatic hydrocarbons.
They act as good corrosion inhibitors, film forming,
dewatering agents and show selective fungicidal and
biocidal activity, either by themselves or in the form of the
acetate of hydrochloride salt.

The water soluble alkali propionates of these long chain
heterocyclic nitrogen compounds have been found to be
detergents in the wet processing of textiles and leather,
excellent wetting and emulsifying agents, dyeing assistants
and finishing compounds.

As petroleum additives, they serve as corrosion inhi-
bitors for aqueous salt and acid solutions, film forming
compounds on metals, dewatering agents, in the mining indus-
try as flotation agents, frothing compounds and selective
mineral wetting agents.

In the pharmaceutical industry, these compounds offer
combined detergency with germicidal properties.

The alkanolic acids of these long chain heterocyclic
nitrogen compounds combine with amines to form both
oil and water soluble emulsifiers with corrosion inhibiting
properties.

EXAMPLE III

\[
\text{C}_3\text{H}_7\text{N} + \text{CH}_3\text{C} = \text{CHCN} \rightarrow \text{C}_3\text{H}_7\text{N} + \text{CH}_3\text{C} = \text{CHCN} 
\]

EXAMPLE IV

\[
\text{HOCClCH\_CHClCH\_ClN} \rightarrow \text{HOCClCH\_CHClCH\_ClN} 
\]

The terminal \(-\text{CH}_2\) group may be replaced by alkali
metal.

In the process of producing the above identified sur-
factants, the following are the important steps:

(a) Slow addition of the acrylate,
(b) The use of methyl acrylate,
(c) The temperature range from 140 to 212° F. or 60°
C. to 100° C.,
(d) The finishing operation at higher temperature,
(e) The stripping of any excess,
(f) The production of 98% yield.

This procedure and the resultant compounds are not
shown in Mannheimer Patent No. 2,528,379, who pro-
duces a dicarboxylic compound of quite different prop-
erties. The dicarboxylic acid is quite different in this re-
spect from the monocarboxylic compound. Moreover,
Mannheimer does not obtain biocidal properties since he
must mix with quaternary ammonium compounds.

Furthermore, Mannheimer has to use chloroaromatic
or sodium chloroacetate which will form a betaine or a qua-
ternary compound in which the 1-nitrogen of the ring
must be quaternized by the chloroacetate as follows:

\[
\text{Cl} + \text{CH}_2\text{COOH} \rightarrow \text{Cl} + \text{CH}_2\text{COOH} 
\]

Therefore, Mannheimer has neither the product, nor
the process of applicant.

Reiberg, Patent No. 2,504,151, describes reacting methyl acrylate with furfuryl alcohol with 30% yield after
24 hours (Example 23). The temperature is below 35°
C. It will be noted that the acrylate is added to the alcohol
in the presence of sodium.

Where in Example 1, a 60% yield is obtained it is
necessary to use a molar ratio of 2 to 8 at a temperature
below 40° C and here again sodium must be used and
the butanol is added.

De Groote, Patent No. 2,468,180, relates to a process
for breaking or resolving petroleum emulsions using
cationic glyoxalides (imidazolines). It discloses the use of di-quaternary ammonium derivatives of fatty imidazo-
lines for use as emulsion breakers. It is no way pertains
to water soluble amphoteric surfactants based on amino
carboxylic acids.
Stromberg, Patent No. 2,987,515, relates to diurethanes of
imidazolines as corrosion inhibitors. These compounds
may have poor or fair corrosion inhibiting properties
quite different from the applicant's. The applicant has
quite different alkyl heterocyclic propionitriles and pro-
pionate esters which are excellent oil soluble corrosion
inhibitors. For example, applicant's compounds which are
water soluble have the unexpected property of corrosion
inhibition in aqueous solution. Steel wool pads, which
normally rust and disintegrate in 24 hours when immersed
in tap water, remain clean and in perfect condition when
the tap water has 1% to 5% of the applicant's products.

EXAMPLE V
1-laurylamidoethoxyethyl piperazine is prepared using methyl acrylate.
One mole of methyl laurate and one mole aminoethoxyethyl
piperazine were added to a three neck flask equipped with
a stirrer, Stark-Dean trap, condenser and thermometer.
The reaction is carried out at 150-215° C. resulting in
a yield of 98% 1-laurylamidoethoxyethyl piperazine (HCl number
205).
The product was cooled to just above its melting point
(65° C.) and one mole of methyl acrylate was added
slowly at this temperature. After the addition of the methyl
acrylate the temperature was raised to 90° C. and the
reaction mass stirred for an additional three hours.
At the end of this time, the tertiary amine content by
the phenyl isocyanate method was 95% of theoretical.
The 1-laurylamidoethoxyethyl piperazine was saponified with one mole of caustic soda dissolved in
one liter of water.
The resulting product was a soft white water soluble
paste. It is amphoteric in nature being soluble in both
acidic and basic solutions and does not precipitate in the
presence of calcium or magnesium ions. The product is
an excellent scouring agent for cotton, rayon, wool and
synthetic fibers.

EXAMPLE VI
1-laurylamido, 4-hydroxyethyl piperazine (93% yield), to
which was added one mole of methyl acrylate as described
in the previous example.
This product was then saponified with aqueous caustic
soda to form a paste containing 33% active matter which
had excellent detergent and wetting properties in both
basic and acidic scouring baths.
Having now particularly described and ascertained the
nature of the invention, and in what manner the same is
to be performed, what is claimed is:
1. A compound, 1-(dodecyl-amidoethyl)-4-carbo-
methoxyethyl-piperazine.
2. A piperazine having the following structural for-
"mula:

\[
\text{CH}_2-\text{CH}_2 \quad \text{N} \quad \text{CH} \quad \text{COOR} \\
\text{CH}_2-\text{CH}_2 \quad \text{O} \quad \text{C}_n \text{H}_m \text{O} \quad \text{COR}
\]

where R is a long chain alkyl group having from 8 to 22
carbon atoms and R_1 is selected from the group consist-
ing of hydrogen and an alkaline metal.
3. A piperazine having the following structural for-
"mula:

\[
\text{CH}_2-\text{CH}_2 \quad \text{N} \quad \text{CH} \quad \text{COOR} \\
\text{CH}_2-\text{CH}_2 \quad \text{O} \quad \text{C}_n \text{H}_m \text{O} \quad \text{COR}
\]

where R is a long chain alkyl group having from 8 to 22
carbon atoms and R_1 is selected from the class consisting of
hydrogen and an alkaline metal.
4. As a compound,

\[
\text{CH}_2\text{H}_3\text{O} \quad \text{N} \quad \text{CH}_2\text{H}_3 \quad \text{COONa}
\]

5. As a compound,

\[
\text{CH}_2\text{O} \quad \text{C} \quad \text{C} \quad \text{H}_3 \quad \text{O} \quad \text{C} \quad \text{H}_3
\]

References Cited
1288-92.
HENRY R. JILES, Primary Examiner.